Quick Fabrication and Thermoelectric Properties of Doped Tetrahedrites

Ping Lv, Yun Yu and Xiaoya Li

Abstract In this paper, the effect of annealing time on the microstructure and thermoelectric properties of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite was studied, hoping to shorten the fabrication time of bulk doped tetrahedrites. The results show that $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite phase formed in the melt during cooling. The ingot consisted of principal phase of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ and secondary phases of Cu_3SbS_4, Cu_2S and $CuSbS_2$. Long time annealing could not eliminate the Cu_3SbS_4 and $CuSbS_2$ phases in $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite. Sintering could eliminate Cu_2S phase. Long time annealing had slight effect on electrical resistivity, and negligible effect on Seebeck coefficient and thermal conductivity of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite. All the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ samples had *ZT* in excess of 0.6 at above 650 K and the maximum *ZT* value obtained in this study was 0.74 for the un-annealed sample. Cobalt doped tetrahedrite $Cu_{11.5}Co_{0.5}Sb_4S_{13}$ fabricated by the un-annealed process could also obtain a *ZT* value of ~ 0.7. Based on the experimental results, the time for preparing doped tetrahedrites can be cut considerably.

Keywords $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite · Annealing · Microstructure Thermoelectric properties

Introduction

With increasing energy consumption and intensifying environmental problems, the environment-friendly thermoelectric technology attracts wide attention as one of the alternative ways to tackle the above mentioned problems. Thermoelectric conver-

P. Lv · Y. Yu
School of Materials and Engineering, Jiangsu University of Technology, Changzhou 213001, China

P. Lv · X. Li (✉)
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
e-mail: xyli@mail.sic.ac.cn

Y. Han (ed.), *Advances in Energy and Environmental Materials*, Springer Proceedings in Energy, https://doi.org/10.1007/978-981-13-0158-2_7

sion efficiency depends on the Carnot efficiency and dimensionless figure of merit, the *ZT* value, defined as $ZT = \alpha^2 T/\rho\kappa$, where α, T, ρ and κ are the Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity, respectively. The performance of thermoelectric materials has made great progress as the advancement of the theories of thermoelectric materials and synthetic preparation [1, 2]. However, the complicated and time- and energy-consuming fabrication process, high cost, toxic elements and the use of rare elements limit large-scale applications of thermoelectric materials.

Tetrahedrite ($Cu_{12}Sb_4S_{13}$) thermoelectric materials consist mainly of earth-abundant and environment-friendly elements copper and sulfur, moreover, natural mineral tetrahedrites can be used as direct source of the thermoelectric materials [3]. Researches on the low-cost, environment-friendly, high performance tetrahedrite thermoelectric materials are expected to create new opportunities of thermoelectric energy generation applications. Till now researches have been mainly focused on the enhancement of the thermoelectric performance of $Cu_{12}Sb_4S_{13}$ tetrahedrite by substitution Cu with Mn, Fe, Co, Ni, Zn and other elements. The highest *ZT* values reported for the Zn, Ni, Ni and Zn, Fe, Mn and Te doped tetrahedrites are 0.9 [3], 0.7 [4], 1.03 [5], 0.8 [3], 1.13 [6] and 0.92 [7], respectively. However, the preparation process of tetrahedrites is time and energy consuming. The melting time is about three days and the annealing time is two weeks [3]. In our previous work [8], a process was developed to prepare undoped tetrahedrite $Cu_{12}Sb_4S_{13}$ with good thermoelectric performance in a considerably reduced melting and annealing time. In this work, the effect of annealing time on the microstructure and thermoelectric properties of Mn doped tetrahedrite $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ was studied, hoping to shorten the fabrication time of bulk doped tetrahedrites. Results show that good thermoelectric performance doped tetrahedrite can also be obtained by a fast preparation process without annealing.

Experimental Procedures

Ten gram $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$tetrahedrite ingots were prepared by a direct melting method. The starting materials, Cu shots (99.999%, Alfa-Aesar), Mn pieces (99.95%, Alfa-Aesar), Sb shot (99.9999%, Alfa-Aesar) and S pieces (99.999%, Alfa-Aesar), were weighed out in stoichiometric ratios and loaded into silica ampoules. The ampoules were evacuated to a pressure of 0.1 Pa and then sealed. The sealed ampoules were suspended in a vertical tube furnace, and heated to 923 K at a rate of 15 $Kmin^{-1}$ and held for four hours. Then the furnace was switched off, and the ampoules cooled down to room temperature.

To study the effect of annealing time on the microstructure and thermoelectric properties of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite, the ingots were crushed and ground into powders, and then cold pressed and placed into silica ampoules and a box furnace to anneal at 723 K for one day, 3, 7 and 14 days, respectively. The annealed pellets were ground into powders, loaded into graphite dies with a

diameter of 15 mm, and then hot pressed at 743 K and 62 MPa for 40 min. For comparison, a disc was also hot pressed under the same condition with the un-annealed powders. The sintered disks were cut for characterization of thermoelectric properties.

The samples were examined by powder X-ray diffraction (XRD, Rigaku Rint 2000, Cu K_α). The microstructure and phase composition of the ingot and sintered samples were also examined by SEM and EDS. The densities of the sintered samples were measured using the Archimedean method. The Seebeck coefficient and electrical resistivity were measured using the standard 4-probe method (LINSEIS LSR-3) in helium atmosphere. The thermal conductivity was calculated from the measured thermal diffusivity D, specific heat $C_{p,}$ and density d according to the relationship $\kappa = DC_pd$. Thermal diffusivity of the samples were measured by a laser flash method (LINSEIS LFA 1000) and the specific heat $C_p$of the samples was calculated using the Dulong-Petit law. The measurement errors for the electrical resistivity, the thermal conductivity and the Seebeck coefficient are ±5–7, ±5–7 and ±5%, respectively.

Results and Discussion

X-ray Diffraction Patterns. For the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$tetrahedrite powder samples are shown Fig. 1 The major peaks of the un-annealed sample match the $Cu_{12}Sb_4S_{13}$ phase, and a few peaks match Cu_3SbS_4, implying that the tetrahedrite phase forms in the melt during cooling, and the ingots consist of principal $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite and secondary Cu_3SbS_4. The annealed samples also contain secondary phase Cu_3SbS_4. Wang [8, 9] and Chetty [10] and Suekuni [11] also observed the secondary phase Cu_3SbS_4 in the synthesized tetrahedrite materials. It seems long time annealing cannot eliminate the second phase Cu_3SbS_4 in tetrahedrites.

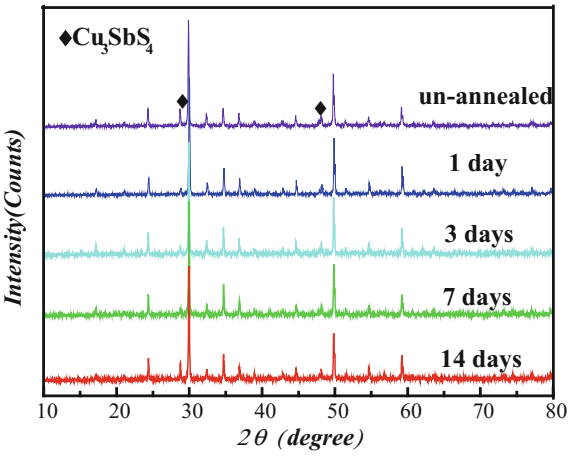

Fig. 1 X-ray diffraction patterns for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite powder samples

SEM Back Scattering Images. of the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite ingot and sintered samples with powders before and after annealing for 1 day and 14 days are shown Fig. 2. It can be seen that the ingot consists of matrix and secondary phases in light grey, dark grey and white. EDS show they are $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$, Cu_3SbS_4, Cu_2S and $CuSbS_2$, respectively. The sintered samples consist of matrix $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ and secondary Cu_3SbS_4 and $CuSbS_2$. The impurity phase $CuSbS_2$ is not found in the X-ray diffraction patterns (Fig. 1). The reason is likely that the content of impurity phase $CuSbS_2$ is too less to be detected, whose diffraction peak is obscured in comparison to the peaks of other phases. The impurity phase Cu_2S in the ingot disappears in the sintered samples, possibly due to the Cu_2S phase reacts further into other phase under high temperature and high pressure during the sintering process. In addition, the micro-porous area fraction of the sample sintered with the one day annealed powders is significantly less than that of the samples sintered with the powders before and after annealed for 14 days. As is known, the longer the annealing time the better the crystallization quality is for the annealed powders. And the better crystallization quality the poorer sintering property is for the annealed powders. This maybe the reason why the sample sintered with the one day annealed powders has less micro-porous in comparison to other samples.

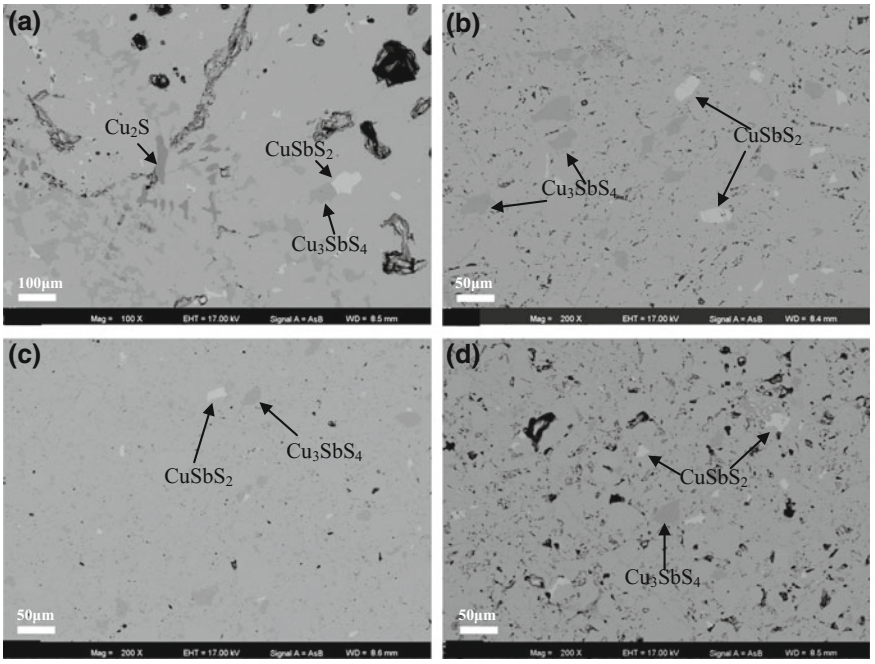

Fig. 2 Back-scattering images of the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ Tetrahedrite ingot (**a**) and samples sintered with powder before (**b**) and after annealing for 1 day (**c**) and 14 days (**d**)

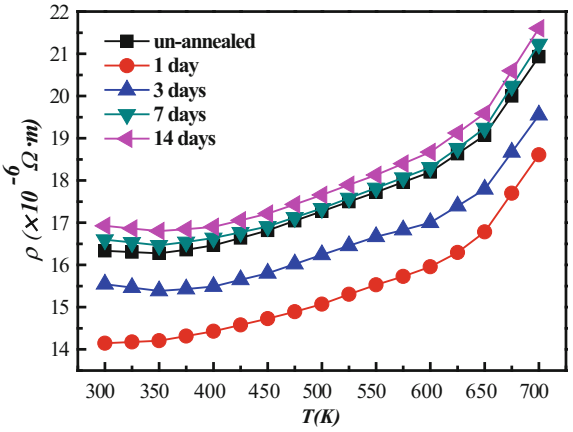

Fig. 3 Temperature dependence of the electrical resistivity for the$Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing

Electrical Conductivity. As a function of temperature for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ samples sintered with powders before and after annealing is shown Fig. 3. The electrical resistivity of all the samples of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ increases with temperature. The tendency of the electrical resistivity change with temperature agrees with that reported by Wang [9] and Chetty [10]. The electrical resistivity of the samples decreases with increase of annealing time, and then increases with increasing annealing time when the annealing time exceeds one day. The electrical resistivity of the un-annealed sample is about 16.335–20.932 $\times$ 10^{-6} Ω m in whole temperature range. The electrical resistivity of the one day annealed sample drops to 14.145–18.608 $\times$ 10^{-6} Ω m, which is the lowest among the samples. And the electrical resistivity goes up to 15.542–19.548 $\times$ 10^{-6}, 16.597–21.228 $\times$ 10^{-6} and 16.928–21.603 $\times$ 10^{-6} Ω m for the 3, 7 and 14 days annealed samples, respectively. The trend of electrical resistivity change with annealing time is inconsistent with that of $Cu_{12}Sb_4S_{13}$ tetrahedrite [8], which goes down with increasing annealing time. The crystallization quality, homogeneity of the doped Mn (the real doping amount) and density combine to affect the electrical resistivity of the samples. As the annealing time increases, the crystallization quality and the homogeneity of the doped Mn are improved, and the density drops slightly under the same sintering condition. The electrical resistivity of the samples decreases with increasing of crystallization quality, and increases with increasing of real Mn doping amount and dropping of density. That's why the electrical resistivity of the samples drops at first, and then increase with increasing annealing time.

Seebeck Coefficient. As a function of temperature for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing is shown in Fig. 4. The Seebeck cofficient of all the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples is positive and rises with temperature, which indicates the majority carriers are hole and the tetrahedrites exhibit p-type conduction. Although the seebeck coefficients of the sample is different, and the difference is small within the measurement error, which means that annealing time has a negligible effect on the seebeck coefficient.

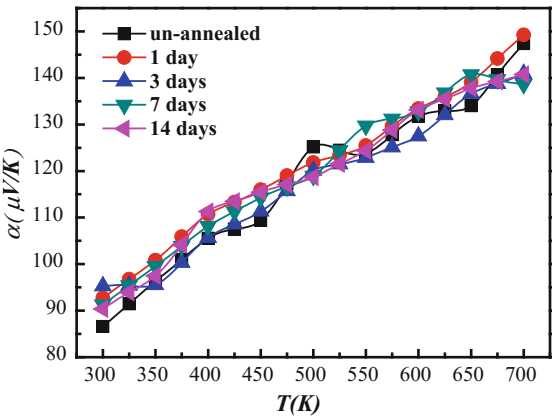

Fig. 4 Temperature dependence of the Seebeck coefficient for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing

In the temperature range of 300–700 K, the seebeck coefficient of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples is between 86 and 150 μV/K, close to that of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrites reported by Wang [9] and Chetty [10].

Thermal Conductivity. As function of temperature for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing is shown in Fig. 5. The thermal conductivity of the samples rises with increasing temperature, and then drops slightly over the temperature range of 650–700 K, similar to those reported before [6, 9, 10]. It was attributed to a low lattice thermal conductivity resulting from complex crystal structure and strong lattice anharmonicity and dominant electronic thermal conductivity which increases with temperature according to Wiedemann-Franz law [7]. Among all the samples, the thermal conductivity of the one day annealed sample is the highest, 1.12–1.22 Wm^{-1} K^{-1}, over the temperature range of 400–700 K, while that of the un-annealed sample is the lowest, 0.96–1.00 Wm^{-1} K^{-1}. The thermal conductivity of the more than one annealed samples is very close, the difference of the thermal conductivity is within the measurement errors, indicating that prolonged annealing time has negligible effect on the thermal conductivity of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite.

Dimensionless Figure of Merit (*ZT*). As function of temperature for all the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples is calculated based on the above data and is presented in Fig. 6. It can be seen that the samples with different annealing time have similar *ZT* value in the temperature range of ~700 K, and the *ZT* value of the samples exceeds 0.6 at above 650 K. Theun-annealed sample has the largest *ZT* value of 0.74, which is very close to that of $Cu_{11.6}Mn_{0.4}Sb_4S_{13}$ tetrahedrite reported by Chetty [10]. This means it is unnecessary to prolong annealing to improve thermoelectric properties of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$tetrahedrite. Cobalt doped tetrahedrite $Cu_{11.5}Co_{0.5}Sb_4S_{13}$ was also prepared by the process of melting and hot press, without annealing. The *ZT* value of the tetrahedrite is ~0.7. It seems that preparation time of high performance doped tetrahedrite thermoelectric materials can be cut considerably.

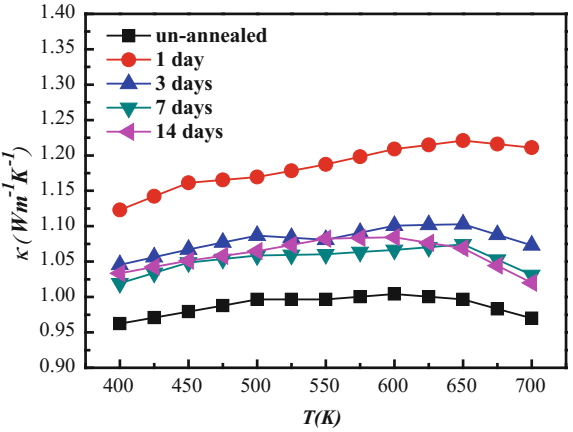

Fig. 5 Temperature dependence of the thermal conductivity for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing

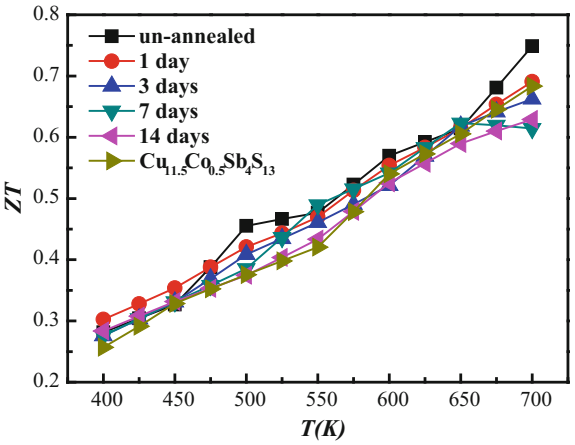

Fig. 6 Temperature dependence of the figure of merit for the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite and $Cu_{11.5}Co_{0.5}Sb_4S_{13}$ tetrahedrite samples

Summary

Manganese doped tetrahedrite $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ was fabricated by fast melting and annealing method. The $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$tetrahedrite phase forms in the melt during cooling. The ingot consists of principal phase of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ and secondary phases of Cu_3SbS_4, Cu_2S and $CuSbS_2$. Annealing has negligible effect on eliminating the Cu_3SbS_4 and $CuSbS_2$ phases in $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite. Sintering can eliminate Cu_2S phase. Long time annealing has slight effect on electrical resistivity, and negligible effect on Seebeck coefficient and thermal conductivity of $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ tetrahedrite. All the $Cu_{11.5}Mn_{0.5}Sb_4S_{13}$ samples have *ZT* in excess of 0.6 at above 650 K and the maximum *ZT* value obtained in this study is 0.74 for the un-annealed sample. Cobalt doped tetrahedrite $Cu_{11.5}Co_{0.5}Sb_4S_{13}$ fabricated by the un-annealed process also obtained *ZT* value of

$\sim$0.7. Based on our experimental results, the time for preparing doped tetrahedrites can be cut considerably.

Acknowledgements This work is financially supported by Natural Science Foundation of China (51372261).

References

1. L.D. Zhao, H.J. Wu, S.Q. Hao, C.I. Wu, X.Y. Zhou, K. Biswas, J.Q. He, T.P. Hogan, C. Uher, C. Wolverton, All-scale hierarchical thermoelectrics: MgTe in PbTe facilitates valence band convergence and suppresses bipolar thermal transport for high performance. Energy Environ. Sci. **6**, 3346–3355 (2013)
2. Y.Z. Pei, X.Y. Shi, A. LaLonde, H. Wang, L.D. Chen, G.J. Snyder, Convergence of electronic bands for high performance bulk thermoelectrics. Nature **473**, 66–69 (2011)
3. X. Lu, D.T. Morelli, Y. Xia, F. Zhou, V. Ozolins, H. Chi, C. Uher, High performance thermoelectricity in earth-abundant compounds based on natural mineral tetradrites. Adv. Energy Mater. **3**, 342–348 (2013)
4. K. Suekuni, K. Tsuruta, M. Kunii, H. Nishiate, E. Nishibori, S. Maki, M. Ohta, A. Yamamoto, M.J. Koyano, High performance thermoelectric mineral $Cu_{12-x}Ni_xSb_4S_{13}$ tetradrites. J. Appl. Phys. **113**, 043712 (2013)
5. X. Lu, D.T. Morelli, Y. Xia, F. Zhou, V. Ozolins, Increasing the thermoelectric figure of merit of tetrahedrite by co-doping with nickel and zinc. Chem. Mater. **27**, 408–413 (2015)
6. J. Heo, G. Laurita, S. Muir, M.A. Subramanian, D.A. Keszler, Enhanced thermoelectric performance of synthetic tetrahedrites. Chem. Mater. **26**, 2047–2051 (2014)
7. X. Lu, D. Morelli, The effect of Te substitution for Sb on thermoelectric properties of tetrahedrite. J. Electron. Mater. **43**, 1983–1987 (2014)
8. J.Y. Wang, M. Gu, Y.F. Bao, X.Y. Li, L.D. Chen, Quick fabrication and thermoelectric properties of $Cu_{12}Sb_4S_{13}$ tetrahedrite. J. Electron. Mater. **45**, 2274–2277 (2016)
9. J.Y. Wang, X.Y. Li, Y.F. Bao, Thermoelectric properties of Mn doped $Cu_{12-x}Mn_xSb_4S_{13}$ tetrahedrites. Mater. Sci. Forum **847**, 161–165 (2016)
10. R. Chetty, P. Kumar, G. Rogl, P. Rogl, E. Bauer, H. Michor, S. Suwas, S. Puchegger, G. Giesterg, R. Mallik, Thermoelectric properties of a Mn substituted synthetic tetrahedrite. Phys. Chem. Chem. Phys. **17**, 1716–1727 (2015)
11. K. Suekuni, K. Tsuruta, T. Ariga, M. Koyano, Thermoelectric properties of mineral tetrahedrite $Cu_{10}Tr_2Sb_4S_{13}$. Appl. Phys. Exp. **5**, 05120 (2012)